Synthesis and Structural Characterisation of Two Novel Gd^{III} β-Diketonates [Gd$_4$(μ$_3$-OH)$_4$(μ$_2$-H$_2$O)$_2$(H$_2$O)$_4$(hfpd)$_8$]·2C$_6$H$_6$·H$_2$O 1 and [Gd(hfpd)$_3$(Me$_2$CO)(H$_2$O)] 2 (hfpd–H = 1,1,1,5,5,5-hexafluoropentane-2,4-dione)

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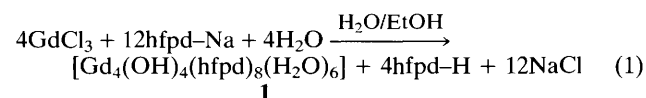
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Two novel Gd^{III}–hfpd complexes 1 and 2 have been synthesised from aqueous and non-aqueous media; the crystal structural studies reveal that 1 has a M$_4$O$_6$ bicapped cubane core with the metals having tricapped trigonal prismatic geometry, while 2 is a monomeric adduct with water and acetone in the coordination sphere, with the metal having square antiprismatic geometry.
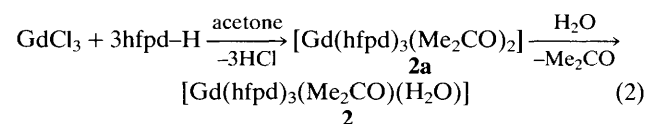
Metallorganic chemical vapour deposition (MOCVD) has been used as an important technique for the preparation of industrially significant thin films; the synthesis and evaluation of suitable molecular precursors[1] is of critical importance. Small changes in the molecular architecture of the ligands will alter oligomerisation, volatility and mass transport of the materials.[2] Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ can be used as electrolyte in solid oxide fuel cells (SOFC).

Tailored molecular precursor synthesis with carefully selected Lewis bases leads to Gd(tmhd)$_3$ (tmhd–H : 2,2,6,6-tetramethylheptane-3,5-dione) adducts with improved mass transport properties when compared with the parent compound.[3] Fluorinated ligands can also lead to products with further improved properties (e.g. melting point, sublimation, vapour pressure). Herein, we report the synthesis and characterisation of two novel complexes derived from two different GdCl$_3$– hfpd–H reaction systems.

The reaction of preformed hfpd–Na and GdCl$_3$ in aqueous–alcoholic media appears to be instantaneous with formation of 1 as a white precipitate [eqn. (1)].

$$4GdCl_3 + 12hfpd{-}Na + 4H_2O \xrightarrow{H_2O/EtOH} [Gd_4(OH)_4(hfpd)_8(H_2O)_6] + 4hfpd{-}H + 12NaCl \quad (1)$$
$$\mathbf{1}$$

In contrast the reaction of GdCl$_3$ with hfpd–H in acetone proceeds very slowly, and removal of the produced HCl is necessary for the completion of the reaction [eqn. (2)].

$$GdCl_3 + 3hfpd{-}H \xrightarrow[-3HCl]{acetone} [Gd(hfpd)_3(Me_2CO)_2] \xrightarrow[-Me_2CO]{H_2O}$$
$$\mathbf{2a}$$
$$[Gd(hfpd)_3(Me_2CO)(H_2O)] \quad (2)$$
$$\mathbf{2}$$

It appears that initially a bis-acetone adduct 2a is formed but its isolation and characterisation are impossible because of its high sensitivity to moisture. The liquid intermediate reacts readily with moist air in n-hexane and produces the complex 2 in the form of large cubes which are also moisture sensitive.

Physical measurements show that while complex 1 is thermally unstable with poor mass transport properties, 2 sublimes at low temperatures.

The use of moist oxygen, as a reacting gas during the deposition experiment, should prevent fluorine incorporation into the film.

The crystal structure of 1 consists of discrete tetranuclear units of [Gd$_4$(μ$_3$-OH)$_4$(μ$_2$-H$_2$O)$_2$(H$_2$O)$_4$(hfpd)$_8$], water and benzene solvents, held together by a network of hydrogen bonds including O–H···O/F as well as C–H···F interactions. The structure of the tetramer which has a crystallographic 2-fold axis of symmetry is illustrated in Fig. 1.† It can be better described as a distorted bicapped cubane, constructed by four gadolinium atoms and four triply bridging hydroxy ligands. A large trigonal dodecahedral distortion of the cube is caused by two bridging water molecules, one on the top and the other at

the bottom of the arrangement, pulling Gd(1) and Gd(1)′ upwards and Gd(2) and Gd(2)′ downwards. The bridging water molecules [O(9) and O(10)] are sited on the C$_2$ axis, with Gd–O distances [2.583, 2.620 Å] in the range for coordinated aqua ligands[4] and considerably longer than the Gd–μ$_3$-OH bonds (average 2.392 Å). Each gadolinium atom is bonded to three μ$_3$-hydroxy ligands, one μ$_2$- and one terminal aqua ligands, and two asymmetrically chelated hfpd ligands in a tricapped trigonal prismatic environment. The capping positions are occupied by O(3), O(9) and O(13) for Gd(1), and O(7), O(10) and O(14) for Gd(2).

Complex 2, shown in Fig. 2, is monomeric with the Gd^{III} atom having an eight coordinate square antiprismatic geometry.† Two of the hfpd ligands are symmetrically chelated to the gadolinium atom (average bond distance 2.376 Å) while the third is asymmetric [Gd–O(5) 2.422(4), Gd–O(6) 2.362(5) Å]. The strong intermolecular hydrogen bonding between the coordinated water and this hfpd ligand appears to
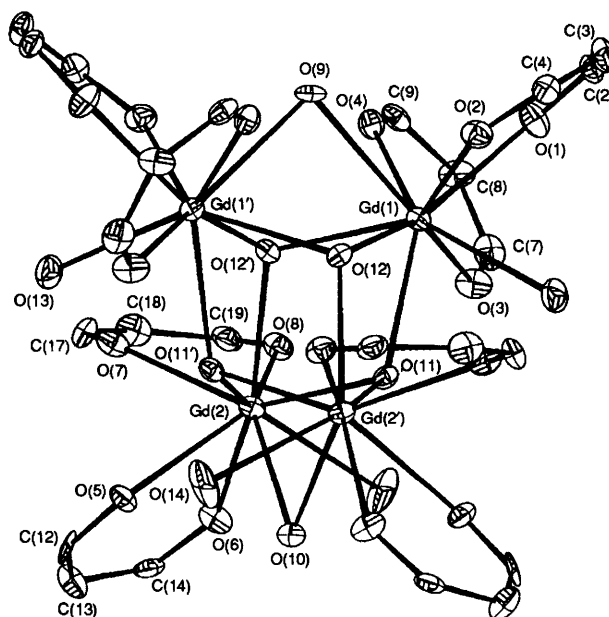

Fig. 1 The structure of 1 viewed perpendicular to the twofold axis. The primed atoms are related by this axis. Trifluoromethyl groups and hydrogen atoms, and solvated molecules have been omitted for clarity. Relevant bonding parameters are: Gd(1)–O(1) 2.392(8), Gd(1)–O(2) 2.445(8), Gd(1)–O(3) 2.372(8), Gd(1)–O(4) 2.447(8), Gd(1)–O(9) 2.584(7), Gd(1)–O(11) 2.407(8), Gd(1)–O(12) 2.412(7), Gd(1)–O(12′) 2.403(7), Gd(1)–O(13′) 2.465(8), Gd(2)–O(5), 2.477(7), Gd(2)–O(6) 2.401(8), Gd(2)–O(7) 2.423(8), Gd(2)–O(8) 2.387(8), Gd(2)–O(10) 2.620(8), Gd(2)–O(11) 2.389(8), Gd(2)–O(11′) 2.368(8), Gd(2)–O(12′) 2.363(7), Gd(2)–O(14′) 2.529(8) Å; Gd(1)–O(9)–Gd(1′) 91.6(3), Gd(2)–O(10)–Gd(2′) 89.1(3), Gd(2)–O(11)–Gd(2′) 101.2(3), Gd(1)–O(11)–Gd(2′) 110.6(3), Gd(1)–O(11)–Gd(2) 108.5(3), Gd(1′)–O(12)–Gd(2′) 109.5(3), Gd(1)–O(12)–Gd(2′) 110.6(3), Gd(1)–O(12)–Gd(1′) 100.6(3)°.
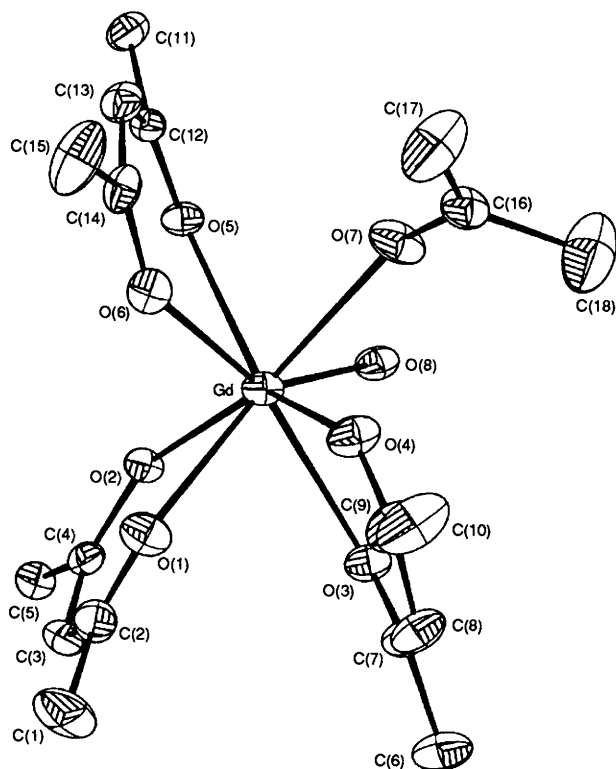
Fig. 2 The structure and labelling scheme for 2. Fluorine and hydrogen atoms have been omitted for clarity. Relevant bonding parameters are: Gd–O(1) 2.375(4), Gd–O(2) 2.396(4), Gd–O(3) 2.378(4), Gd–O(4) 2.354(4), Gd–O(5) 2.422(4), Gd–O(6) 2.362(5), Gd–O(7) 2.404(4), Gd–O(8) 2.422(4) Å; O(1)–Gd–O(2) 71.9(2), O(3)–Gd–O(4) 71.8(2), O(5)–Gd–O(6) 71.6(1), O(7)–Gd–O(8) 76.8(2)°.

be responsible for this behaviour. The Gd–O$_{(H_2O)}$ and Gd–O$_{(acetone)}$ distances, 2.404 and 2.411 Å, respectively, are in the range expected for neutral Lewis bases.

To our knowledge these structural types are quite unique in lanthanide chemistry with a number of novel features: (i) Although the structural chemistry of hfpd–H has been studied to some extend with transition[5a] and alkaline earth[5b] metals, examples of structurally characterised Ln^{III}–hfpd complexes are scarce in the literature. (ii) Compound 1 is the first tetranuclear lanthanoid complex with a cubane arrangement. In most of tetranuclear lanthanoid complexes the arrangement of the four metals is planar, the structure being supported by only two triply bridged hydroxide ligands.[6] (iii) Bridging water molecules occur in several crystal hydrates, but ternary complexes with bridging aqua ligands are very few.[7]

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